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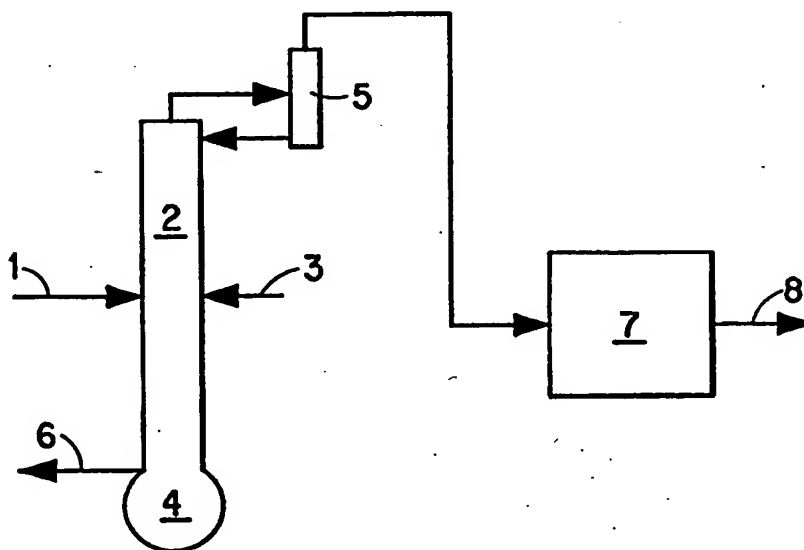
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(54) Title: MANUFACTURE OF 1,1-DIFLUOROETHANE BY REACTIVE DISTILLATION

(57) Abstract

A process is disclosed for purifying 1,1-difluoroethane (HFC-152a) by reactive distillation. In one aspect the process removes unsaturated species and chlorinated organic impurities from HFC-152a by either hydrofluorination or halogen substitution while simultaneously distilling off the 1,1-difluoroethane product.



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TITLE

Manufacture Of 1,1-Difluoroethane By Reactive Distillation

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Field Of The Invention

The instant invention relates to a process for purifying 1,1-difluoroethane (HFC-152a) by reactive distillation. In one aspect, the instant invention removes unsaturated species and chlorinated organic impurities from HFC-152a by either hydrofluorination or halogen substitution while distilling off the 1,1-difluoroethane product.

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Background

Dihaloethanes can be manufactured by using a wide range of processes. Examples of such processes are described in Golubev et al. (Soviet Inventor Certificate No. 341788).

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Guofei et al. (Chinese Patent Application Publication No 1069019a) discloses using both a water scrubber and caustic scrubber to remove acid from a 1,1-difluoroethane product stream.

Tatsuya et al. (Japanese Patent Application Kokou Publication No JP-48-16487) discloses a method for purifying 1-chloro-1-fluoroethane by absorbing and dissolving in a chlorinated hydrocarbon.

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Mao et al. (Chinese Patent Application Publication No. 1074434 A) discloses using a photochlorination reaction to purify 1,1-difluoroethane.

Brock et al. (U.S. Patent No. 3190930) discloses a process for producing 1,1-difluoroethane from acetylene.

25

The disclosure of the above-identified publications is hereby incorporated by reference.

Summary

Hydrofluorocarbons (HFCs) such as 1,1-difluoroethane can be an environmentally acceptable replacement for certain chlorofluorocarbons (CFCs). 1,1-difluoroethane (CHF_2CH_3 or HFC-152a) may be employed alone or in blends as a refrigerant, cleaning agent, blowing agent for thermoplastic or thermoset foams, an aerosol propellant, a heat transfer media, gaseous dielectrics, power cycle working

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fluids, polymerization media, particulate removal fluids, carrier fluids, buffing abrasive agents, displacement drying agents, an intermediate for making other fluorinated compounds such as vinyl fluoride, among other applications. 1,1-difluoroethane (HFC-152a) can be made by reacting chloroethene ($\text{CH}_2=\text{CHCl}$ or vinyl chloride) with anhydrous hydrofluoric acid either by a liquid or gas phase reaction. For example, HFC-152a can be made by reacting vinyl chloride and HF in a liquid phase wherein a catalyst such as SnCl_4 has been added to the liquid phase. Intermediates or by-products to this reaction may include 1-chloro-1-fluoroethane (HFC-151a), 1,1-dichloroethane (HCC-150a), fluoroethene ($\text{CH}_2=\text{CHF}$ or vinyl fluoride), ethene, among others. The intermediates, by-products, and unreacted starting materials can be impurities in the HFC-152a product.

The instant invention solves problems associated with conventional practices by producing purified HFC-152a while minimizing the generation of additional waste products, e.g., tars. That is, conventional practice typically employ solvents, photochlorination, separate reactions followed by additional purification steps, among other procedures for removing impurities from HFC-152a. These additional purification steps result in increased processing losses and form further amounts of undesirable waste products. The instant invention also solves problems associated with conventional practices by providing a method for obtaining high purity HFC-152a which is substantially free of unsaturated impurities, e.g., containing less than about 100 ppm of vinyl chloride (and preferably less than 10 ppm vinyl chloride). The instant invention solves these problems by using a reactive distillation process.

The inventive reactive distillation process for purifying HFC-152a has several advantages such as an increased yield of HFC-152a since the intermediates can be converted into product, the removal of toxic or other undesirable impurities, e.g., by being converted into more desirable compounds, among other advantages.

The process of the instant invention relates to purifying 1,1-difluoroethane by reactive distillation, and more specifically, to removing unsaturated species and chlorinated organic impurities from HFC-152a by either hydrofluorination or halogen substitution of such impurities while simultaneously distilling off the desired HFC-152a product.

CROSS REFERENCE TO RELATED PATENT APPLICATIONS

The subject matter of the instant invention is related to U.S. Patent Application Serial No. 08/468,099 (Attorney's Docket No. CH-2511), filed on June 5, 1995, in the names of Maria U. D. Beug-Deeb et al., and entitled "Azeotropic and
5 Azeotrope-like Compositions of HF and Dihaloethanes".

The subject matter of the instant invention is also related to U.S. Patent Application Serial No. 08/474,884 (Attorney's Docket No. CH-2512), filed on even date herewith, in the name of Klaus G. Wuttke, and entitled "Continuous Manufacture Of 1,1-Difluoroethane".

10 The subject matter of the instant invention is also related to U.S. Patent Application Serial No. 08/476,770 (Attorney's Docket No. CH-2529), filed on even date herewith, in the names of Mario J. Nappa et al, and entitled "Two-Step Process For Manufacturing 1,1-Difluoroethane".

15 The disclosure of the cross-reference patent applications is hereby incorporated by reference.

Brief Description Of Drawings

FIGURE 1 - Fig. 1 is a schematic diagram of an HF recycle column which can be used in one aspect of the invention to purify HFC-152a by reactive
20 distillation.

FIGURE 2 - Fig. 2 is a schematic diagram of another reactive distillation system that can be used in an aspect of the invention to purify HFC-152a.

Detailed Description

25 The instant invention relates to a reactive distillation process that removes undesired impurities from HFC-152a while improving the HFC-152a yield. Crude HFC-152a produced in either a liquid or vapor phase system can contain up to 5 mole % or more each of vinyl chloride, HCFC-151a, and HCC-150a on an organic basis. Purification by using a reactive distillation process offers several advantages such as
30 increasing the product yield by converting the intermediates into product, breaking azeotropic or azeotrope-like compositions by altering one or more of the azeotrope components, removing toxic or other undesirable impurities, among other advantages.

This invention relates to purifying 1,1-difluoroethane by reactive distillation, and more specifically, to removing unsaturated species and chlorinated

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organic impurities by either hydrofluorination and/or halogen substitution while distilling off the 1,1-difluoroethane product. This process can also be enhanced by using a suitable catalyst.

5 "Conventional distillation" refers to a process wherein the relative volatility of the components in the mixture to be separated is being used for the separation. In comparison to conventional distillation, "reactive distillation" is a process wherein one or more catalyzed or uncatalyzed reactions takes place in the distillation equipment while the desired product is recovered, e.g., as an overhead product from the distillation column. During such a reactive distillation process, the
10 desired product can be removed continuously while converting unreacted starting materials and intermediates into the desired product. For example, HCFC-151a and fluoroethene are converted to HFC-152a, and HCC-150a and chloroethene are converted to HCFC-151a which in turn can form HFC-152a. The reactive distillation process increases the desired product yield and reduces the quantity of unreacted and
15 by-products thereby reducing recycle and separation equipment costs. For example, chloroethene can be converted into HCFC-151a which can in turn be converted into HFC-152a thereby avoiding the presence of a toxic material in the desired HFC-152a product.

Reactive distillation may be performed in a multi-stage distillation
20 column with one or several feed points, a reboiler, an overhead condenser for returning reflux to the column, among other commercially available apparatus. The distillation column that can be employed to carry out the inventive reactive distillation can include various types of internal structures which promote appropriate contact between the vapor and the liquid phases within the column. These structures can include one or
25 more of packings such as dumped packings, e.g., Pall-rings, Raschig rings, Intalox saddler, among others, as well as structured packings such as one or more of Koch, Sutzer, among others. Such structures produce an enhanced surface area per unit volume of packed space to promote phase contacting. The distillation column can also house trays or plates that are constructed to increase liquid residence time or hold-up on
30 the trays or plates, and promote gas dispersion through the liquid. The construction of these trays or plates include one or more of 1) bubble caps comprising a riser, which provides a liquid seal for the tray, and a cap covering the riser that includes a slot for dispersing the vapor through the liquid, 2) perforations in the tray whereby liquid is maintained on the tray by kinetic energy of the vapor passing through the tray, among

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other suitable means for effectively providing liquid/vapor contact. Generally, it is practical to employ a reactive distillation column equipped with trays since trays cause an increase in the residence time of an HF containing liquid within the column thereby permitting relatively large quantities of unreacted starting materials and intermediates to be converted into HFC-152a.

To most effectively remove impurities from HFC-152a, the distillation column should be designed and operated under conditions which create a region within the column that contains a sufficient concentration of HF to accomplish the desired reactions, e.g., as discussed below in greater detail such a region is below the column temperature break point. By sufficient concentration of HF, it is meant that an amount of HF is present to convert at least one of vinyl chloride, HCC-150a and HCFC-151a to HFC-152a. Typically, such a concentration exists below the break point, e.g., below the break point the HF concentration is greater than above the break point. A crude HFC-152a stream can be introduced into or near this HF containing region in a manner so that the desired reactions can occur in the liquid phase progressively along the length of the column. For example, a liquid phase consisting essentially of HFC-152a impurities and HF is maintained upon the trays or packing within the column for a time sufficient to convert at least a portion of the impurities to HFC-152a.

The "break point" in a reactive distillation column is defined as the location along the length of the column at which there is the greatest variation in temperature from stage to stage. The location of this break point is typically controlled either directly or indirectly by the reflux ratio. The location of the break point can affect the degree to which impurities will be reacted, and the location at which crude HFC-152a is introduced into the reactive distillation column. That is, introducing the crude HFC-152a stream into the column at a location below the break point ables the crude HFC-152a stream to be contacted with the increased levels of HF present thereby converting the impurities into more desirable compounds.

When introducing crude HFC-152a into the reactive distillation column, the predominate compounds are HF and typically equimolar quantities of HFC-152a and HCl, and impurities. The region below the break point becomes relatively rich in HF (the high boiling compound) and relatively depleted in HCl (the lower boiling compound). That is, HF has a tendency to travel downwardly through the column. Such a region favors the reactive distillation of one or more of chloroethene, HCC-150a and HCFC-151a to HFC-152a. The conditions in this HF rich region of the distillation

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column are more favorable than the other regions of the reactive distillation column for the essentially complete removal of chloroethene, HCC-150a, and HCFC-151a from HFC-152a, e.g., a crude HFC-152a stream containing up to 5 mole % or more each of vinyl chloride, HCC-150a, HCFC-151a on an organic basis can be converted into an HFC-152a stream substantially free of these impurities. Substantially all of the HFC-152a that was obtained from the impurities exits as an overhead product from the column (along with HFC-152a originally present in the crude stream).

The reactive distillation can be accomplished with or without the presence of a catalyst. That is, the aforementioned conversions and reactions can occur in the reactive distillation column at normal process conditions without the aid of a catalyst. However, any suitable catalyst can be used to accelerate the hydrofluorination and fluorine substitution reactions, e.g., one or more of BF_3 , SnCl_4 , a bifluoride catalyst, chrome oxide, e.g., Cr_2O_3 , among others. Examples of a bifluoride catalyst include sodium fluoride, cesium fluoride, and ammonium fluoride. Alternatively, the catalyst can be made in situ by reacting a Lewis base with HF, for example, the reaction of amines with HF.

To catalyze the reactive distillation with BF_3 , an effective amount of BF_3 is fed into the bottom of the column, e.g., about 0.1 to about 1.0 mole % BF_3 based upon column feed and typically about 0.25 mole %. Since BF_3 is volatile under the reactive distillation conditions, BF_3 can appear in the gas exiting the distillation column. BF_3 can also react with any trace moisture that enters with the feeds to form a high boiling adduct. For best results, BF_3 is usually fed continuously into the reactive distillation column at a location which is below the break point. Any catalyst exiting the reactive distillation column can be separated from the product stream either by conventional distillation or by scrubbing methods, or recycled back into the column.

In some cases, the reactive distillation is performed in the presence of a liquid catalysts such as SnCl_4 . The liquid catalyst can be introduced into the reactive distillation column by being introduced upon the trays or packing in the distillation column. For example, liquid distributors known in this art can be employed to form a substantially uniform coating of the liquid phase across the trays or packing. If desired solid catalysts such as at least one of AlF_3 and Cr_2O_3 , can be packed into specific sections of the column, e.g., AlF_3 can be packed within or external to a stage distillation column.

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The residence time of the crude HFC-152a stream in the HF-rich region of the column, and desired reflux ratio are greater without the use of a fluorination catalyst. When in the presence of a fluorination catalyst, such as BF₃, the region within the column, which is employed for converting impurities to HFC-152a, can be reduced in size that in turn permits operation of the column at lower reflux ratios. The specific residence time, however, is a function of the column design, trays and packings.

Referring now to the Figures, Figure 1 is a schematic diagram of one aspect of the invention. A crude HFC-152a stream comprising one or more of chloroethene, HCC-150a, HCFC-151a, HF, HCl, among others, is transported via conduit 1, and is introduced at any suitable point along the length of the distillation column 2. For best results, the introduction point of the crude HFC-152a stream is below the break-point thereby maximizing the amount of chloroethene, HCC-150a and HCFC-151a that are converted into HFC-152a. The crude HFC-152a stream can be either gaseous, liquid, or a combination of gaseous and liquid.

Additional anhydrous hydrofluoric acid, e.g., containing less than about 0.005 to 0.1 wt % water, can be added into the column either as a separate conduit or feed point 3, or mixed with the HFC-152a feed prior to being introduced into column 2. While feed point 3 can be located at any suitable location, typically it is connected to column 2 at a location higher than where conduit 1 is connected to column 2. Consequently, feed point 3 is also located above the break-point. The total amount of HF present in the column ranges from less than 1% by wt near the column top to about 99% near the column bottom.

In some cases, a catalyst such as BF₃ is used to accelerate the reactions within the distillation column, e.g., converting intermediate products into HFC-152a. A relatively volatile catalyst can be added to the reactive distillation column at any suitable location such as in the vapor space known as a stillpot 4 whereas a less volatile catalyst such as SnCl₄ can be present in conduit 1 and/or added via feed point 3. The amount of catalyst can be about .01 to about 1.0 mole % based upon column feeds. At least a portion of the impurities in the HFC-152a feed can react with HF while in the presence of a catalyst, such that the gas stream exiting reactive distillation column 2 and entering a reflux condenser 5 consists essentially of HFC-152a and HCl, e.g., about equimolar quantities of HCl and HFC-152a. The reflux condenser 5 has a reflux ratio of about 2 to about 15, and is normally operated at a temperature of about 30 to about 50 C. In the event, the gas exiting reactive distillation column 2 contains an excessive

amount of undesired material it can be recycled back to column 2 or transported to another column (not shown).

The HFC-152a stream exiting condenser 5 can be processed further by being transported to scrubber/drier 7. Scrubber/drier 7 can remove residual acids such as HF and HCl thereby producing a high purity HFC-152a stream 8, e.g., essentially free of vinyl chloride, HCC-150a and HCFC-151a. Alternatively or in addition to scrubber/drier 7, the HFC-152a gas stream exiting reflux condenser 5 can also undergo further purification such as being distilled, deacidified by using an aqueous solution comprising NaOH, among other known deacidification/purification techniques, to remove undesired materials.

Materials such as HCFC-151a, HCC-150a, HF, among others can exit from the bottom of the column 2 via conduit 6. These materials can be recycled to a reactor for making HFC-152a, reactive distillation column 2 and/or disposed of as a waste material.

Referring now to Figure 2, Fig. 2 illustrates schematically another system that can be employed to perform one aspect of the inventive reactive distillation process. The apparatus employed in this system are known to those skilled in this art. A reactor 10 is in fluid connection with a reflux column 12. The reaction mass within reactor 10 can be agitated by using a mechanical mixer and/or turbulence caused by gas bubbles within the reaction mass. A crude HFC-152a product stream comprises HFC-152a, chloroethene, HCC-150a, HCFC-151a, HF, HCl, among others, exits the reactor 10, travels via conduit 11, and enters the reflux column 12 that is operated at a reflux ratio between about 2 and 15, a temperature of about 50 to 150 deg. C and a pressure of about 50 to 400 psig. If desired, additional quantities of HF can be added at a separate feed point 13 along the length of the column 12. Feed point 13 is located above the break point along the length of column 12 thereby maximizing the interaction between HF and impurities within the crude HFC-152a stream. Reflux column 12 is connected to reflux condenser 14 which is operated at a temperature of about 30 to about 50 C. Impurities in the HFC-152a feed within column 12 react with HF such that the stream leaving the reflux condenser 14 consists essentially of equimolar amounts of HFC-152a and HCl. A liquid comprising HCFC-151a, HCC-150a, HF, and reduced quantities of HFC-152a, HCl and vinyl chloride, e.g., trace amounts, is transported via conduit 15 from the bottom of the reflux column 12 to reactor 10. By transporting this liquid or

heel to the reactor 10, the inventive process can avoid tar build-up in the reflux column and increase HFC-152a yield.

The specific conditions that can be used for practicing the invention depend upon a number of interrelated design parameters such as the diameter of the column, selected feed points, the number of separation stages in the column, among
5 other parameters. The column should be designed to insure sufficient residence time to complete the conversion or removal of undesired unsaturated compounds. An average residence time of at least about 6 minutes (based on the column feed) was found to be effective, e.g., a residence time that ranges from about 1 to about 30 minutes. The
10 operating pressure of the distillation system may range from about 30 to about 350 psia. The temperature within the distillation column typically ranges from about 30 to about 120 C. The reflux ratio is defined as the ratio of the material at the top of the distillation column which is then condensed and in turn returned to the column, to the amount of material that is removed as product. The reflux ratio also defines the
15 physical characteristics of the distillation column. In general, an increase in the reflux ratio will in turn cause an increase in the product purity. Typically, the reflux ratio ranges from about 2 to about 15.

For best results, the production equipment and its associated feed lines, effluent lines and associated units should be constructed of materials resistant to HF
20 and HCl. Typical materials of construction, well-known to the fluorination art, include stainless steels and the well-known high nickel alloys, such as Monel® nickel-copper alloys, Hastelloy® nickel-based alloys and, Inconel® nickel-chromium alloys.

While the previous description places particular emphasis upon removing impurities from a crude HFC-152a containing stream, the instant invention can be
25 employed for treating a wide range of impure product streams. The instant invention can use HF within a reactive distillation column to affect one or more hydrofluorination reactions, e.g., impurities or residual reactants are contacted with HF for conversion into a desired final product. For example, the instant invention can convert a crude stream containing $\text{CH}_2=\text{CCl}_2$ (HCFC-141b) into a purified HCFC-141b stream, and/or
30 into a stream containing one or more of $\text{CH}_3\text{CF}_2\text{Cl}$ (HCFC-142b), CH_3CF_3 (HFC-143a), and HCl.

Specific examples illustrating the invention are given below. It is to be understood that these examples are merely illustrative and in no way are to be interpreted as limiting the scope of the invention.

Example 1

Reactive Distillation without a Catalyst

This Example illustrates a reactive distillation process that employed the apparatus illustrated in Figure 2.

A reflux column of conventional design (316 S/S) was packed with 5/8 inch Pall rings and operated at approximately 160 psig and a reflux ratio of about 5. The temperature of the column bottom was about 84 deg. C and the top ranged from about 44 to about 45 deg. C. A crude HFC-152a feed stream comprising several impurities and HF was introduced into the bottom of the column below the break point. The concentration profiles of the feed stream impurities present in conduit 11 of Figure 2, the column overhead leaving the reflux condenser 14 and the liquid return from the conduit 15 are given in Table 1 below.

TABLE 1

Feed (by mole)	Top of column (by mole)	Liquid return (by mole)
Chloroethene 128 ppm	25 ppm	2 ppm
HCC-150a 4.23 %	0.031 %	3.20 %
HCFC-151a 5.31 %	0.016 %	1.86 %

For all three impurities, the concentration in the feed is greater than the streams leaving the column. That is, the column was effective at reducing the amount of impurities such that the HFC-152a exiting as an overhead product had been purified. This Example also demonstrates that the impurities in the crude HFC-152a stream were removed by reacting with HF, e.g., HCC-150a was converted to HCFC-151a which was in turn converted to HFC-152a.

Example 2

Reactive Distillation with BF₃

This Example illustrates a reactive distillation process that employed the apparatus illustrated in Figure 1.

An Inconel® distillation column of conventional design and having a 1 inch diameter, 4 ft. rectification section, 8 inch stripping section was packed with 0.09 x 0.175 x 0.175 nickel Heli-Pak™ packing. The column was connected to a steam-heated reboiler or still pot, and the overhead product exiting from the column was transported to a water-cooled condenser. A catalyst comprising BF₃ was added to the column in the vapor space of the stillpot at a rate of approximately 0.26 mole % based upon column feed.

The conditions within the column were approximately as follows: 200 psig pressure and at a bottom column temperature of 111 C and top column temperature of 42 C. The feed point was located near the bottom of the column and below the break point to ensure that the crude HFC-152a was introduced into the column at a region containing an adequate concentrations of HF. The concentration profiles of the feed stream 1, as shown in Figure 1, to the column 2, the column overhead leaving condenser 5 and the heel in conduit 6 are given in Table 2 below:

TABLE 2

		Feed (by mole)	column overhead: (by mole)	Heel: (by weight)
20	Ethene	554 ppm	---	---
	Fluoroethene 50 ppm	---	---	---
	vinyl chloride	0.438%	---	---
	HCC-150a	101 ppm	---	---
	HCFC-151a	0.519 %	341 ppm	---
25	HFC-152a	.55 %	37.6 %	---
	HFC-161	---	306 ppm	---
	HCl	9.42 %	62.0 %	---
	HF	81.8 %	0.35 %	99.5 %
	Misc. organics	---	---	0.132 %
30	Tar	---	---	0.405 %

While chloroethene (vinyl chloride), fluoroethene, and HCC-150a were components of the crude HFC-152a stream that was introduced into the column, none were detected either overhead or in the heel of the column. The amount of HCFC-151a

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was also greatly reduced. Without wishing to be bound by any theory or explanation, it is believed that the appearance of HFC-161 at the top of the column is caused by hydrofluorinating ethene.

The reflux ratio, which was calculated from an enthalpy balance on the top of the column, was about 6.4. The reflux ratio may vary due to heat losses from the column.

Comparative Example

Reactive distillation without a catalyst

The distillation column described in Example 2 and illustrated in Figure 1 was packed with 0.09 x 0.175 x 0.175 nickel Heli-Pak™ packing. The column was connected to a steam-heated reboiler, and the column was connected to a water-cooled condenser.

The conditions within the column were approximately as follows: 200 psig pressure and at a bottom column temperature of about 110 C and a top column temperature of about 41 C. The concentration profiles of the feed stream 1, as shown in Figure 1, to the column 2, the column overhead leaving condenser 5 and the heel in conduit 6 are given in Table 3 below:

20

TABLE 3

	Feed (by mole)	column overhead : (by mole)	Heel: (by weight)
Ethene	603 ppm	---	---
25 Fluoroethene	54 ppm	---	---
chloroethene	0.37%	---	---
HCC-150a	339 ppm	---	---
HCFC-151a	0.34 %	70 ppm	---
HFC-152a	7.49 %	38.1 %	---
30 HFC-161	---	246 ppm	---
HCl	9.46 %	61.5 %	---
HF	82.3 %	0.369 %	99.6 %
Misc. organics	---	---	0.254 %
Tar	---	---	0.173 %

Similar to the results obtained by Example 2, substantially no chloroethene, fluoroethene, and HCC-150a were detected either overhead or in the heel of the column. The amount of HCFC-151a was also greatly reduced, and HFC-161
5 appeared at the top of the column .

The calculated reflux ratio of the distillation column was approximately 7.9.

Example 2 and the above Comparative Example illustrate that in order to substantially completely react the chloroethene and other impurities in the column
10 without the presence of a catalyst, the break-point temperature should be maintained below the middle of the column. Such can be achieved by using a reflux ratio of about 8. However, when BF₃ was introduced into the column (as shown in example 2), the reflux ratio can be reduced to 6.4 while achieving desirable results, e.g., substantially
15 no chloroethene exited the column as an overhead product.

THE FOLLOWING IS CLAIMED:

1. A process for purifying a hydrofluorocarbon containing stream comprising:
5 introducing said stream into a distillation column,
contacting said stream with HF for a time and under conditions sufficient to convert at least a portion of impurities within said stream to hydrofluorination products,
10 recovering a purified hydrofluorocarbon.
2. The process of Claim 1 wherein the hydrofluorocarbon comprises 1,1-difluoroethane.
3. The process of Claim 1 wherein said impurities comprise at least one
15 member from the group of HCC-150a, HCFC-151a and vinyl chloride.
4. The process of Claim 1 wherein said introducing is below the break point of the column.
- 20 5. The process of Claim 1 wherein said contacting is performed within a reactive distillation column under reflux conditions.
6. A process for removing impurities from a stream comprising HFC-152a and at least one impurity comprising a member selected from HCC-150a, HCFC-
25 151a and vinyl chloride, the process comprising the steps of:
introducing said stream into a reactive distillation column under reflux conditions,
contacting said stream with HF wherein said at least one impurity is converted into HFC-152a,
30 recovering an HFC-152a containing stream as an overhead product from the reactive distillation column wherein the HFC-152a containing stream has a reduced quantity of impurity, and;
optionally recycling any remaining impurities to the reactive distillation column.

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7. The process of Claim 1 or 6 wherein HF is added to the column.
8. The process of Claim 1 or 6 wherein said contacting is performed in
5 the presence of a catalyst.
9. The process of Claim 8 wherein said catalyst comprises BF₃ or SnCl₄.
10. The process of Claim 1, 2, 3 or 6 wherein the recovered HFC-152a
10 containing stream comprises about equimolar amounts of HFC-152a and HCl.

1/1

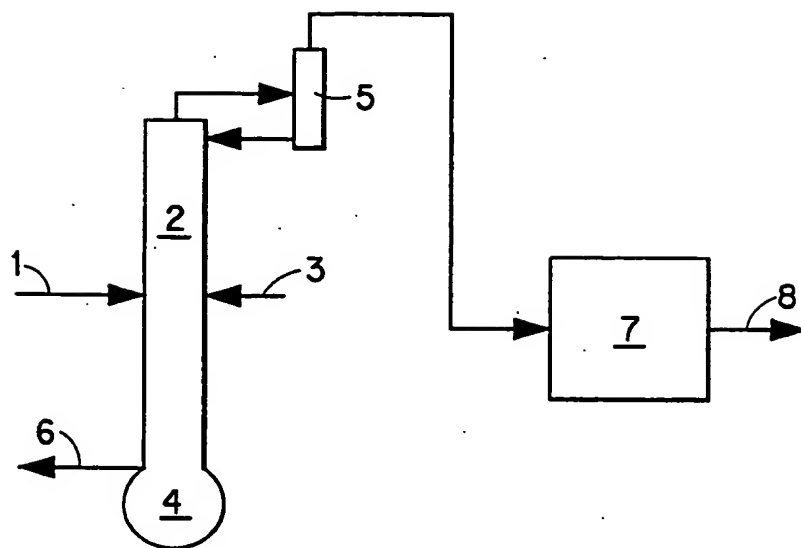


FIG. 1

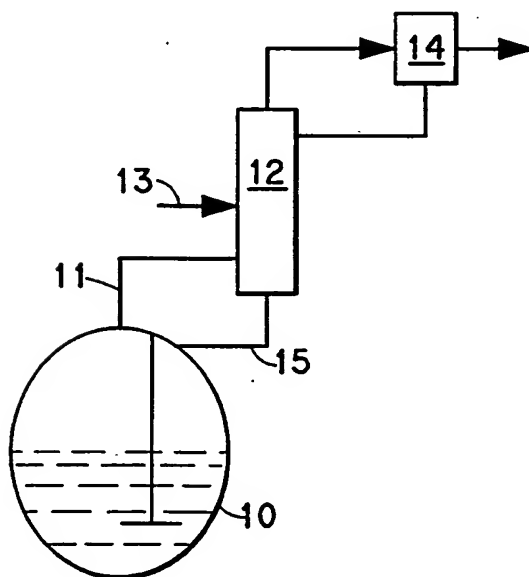


FIG. 2

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INTERNATIONAL SEARCH REPORT

Intern: Application No
PCT/US 96/09234

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C07C17/386 C07C19/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CHEMICAL ABSTRACTS, vol. 078, no. 1, 8 January 1973 Columbus, Ohio, US; abstract no. 003663, GOLUBEV A N ET AL: "1,1-Difluoroethane" page 308; column 1; XP002013161 see abstract & SU,A,341 788 (A.N. GOLUBEV) 14 June 1972 -----	1-3

☐ Further documents are listed in the continuation of box C.

☐ Patent family members are listed in annex.

* Special categories of cited documents :

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Date of the actual completion of the international search

12 September 1996

Date of mailing of the international search report

20.09.96

Name and mailing address of the ISA
European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,
Fax (+ 31-70) 340-3016

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Bonnevalle, E

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